OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0670

TECHNICAL REPORT NO. 2

ON THE DEFICIENCIES OF THE FERRICINIUM-FERROCENE REDOX COUPLE FOR ESTIMATING TRANSFER ENERGIES OF SINGLE IONS

by

Saeed Sahami ▄▄ Michael J. Weaver

Prepared for Publication

in the

Journal of Solution Chemistry

Department of Chemistry

Michigan State University

East Lansing, Mich. 48824

15 Aug 80

80 9 23 032

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER 2	2. GOVT ACCESSION NO. AD-A089 388	3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
ON THE DEFICIENCIES OF THE FERRICINIUM-FERROCENE REDOX COUPLE FOR ESTIMATING TRANSFER ENERGIES OF SINGLE IONS.	Technical Report #2
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
S. Sahami, M. J. Weaver.	N00014-79-C-0670

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Dept. of Chemistry, Michigan State University, East Lansing, Mich. 48824	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research	August 15, 1980
Dept. of the Navy	13. NUMBER OF PAGES
Arlington, Virginia, 22217	14

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

FERRICINIUM-FERROCENE, ION TRANSFER ENERGIES, REACTION ENTROPIES, FORMAMIDE, N-METHYLFORMAMIDE, PROPYLENE CARBONATE, ACETONITRILE, DIMETHYLSULFOXIDE, DIMETHYLFORMAMIDE, NITROMETHANE.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The difference between the partial molal entropies of ferrocene and ferricinium $(\bar{S}^0_{Fc} - \bar{S}^0_{Fc+})$ has been determined in nine solvents from the temperature dependence of the formal potential of the ferricinium-ferrocene redox couple using a nonisothermal electrochemical cell arrangement in order to probe possible structural reasons for the limitations of the
(continued on next page)

DD FORM 1473 EDITION OF 1 NOV 68 IS OBSOLETE
1 JAN 73
S/N 0102-014-6601 |

20. (cont.)

"ferrocene assumption" for estimating the transfer thermodynamics of single ions between different solvents. In contrast to the uniformly small positive values of $(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc^+})$ predicted by the Born model, the experimental quantities varied widely from small or even negative values in hydrogen-bonded solvents (-5 to 3 e.u.) to substantially larger values (11-14 e.u.) in dipolar aprotic media. These variations appear to arise chiefly from additional solvent ordering in the vicinity of the ferricinium cation compared to the ferrocene molecule which is enhanced in the aprotic solvents. The variations in $(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc^+})$ between water and a number of nonaqueous solvents provide a predominate contribution to the differences between the free energies of single ion transfer calculated using the ferrocene and alternative extrathermodynamic assumptions.

PARTIAL MOLAL ENTROPIES OF FERROCENE AND FERRICINIUM

ON THE DEFICIENCIES OF THE FERRICINIUM-FERROCENE REDOX COUPLE

FOR ESTIMATING TRANSFER ENERGIES OF SINGLE IONS

Saeed Sahami and Michael J. Weaver*

Department of Chemistry
Michigan State University
East Lansing, Mich. 48824

Abstract

The difference between the partial molal entropies of ferrocene and ferricinium $(\bar{S}^{\circ}_{Fc} - \bar{S}^{\circ}_{Fc^+})$ has been determined in nine solvents from the temperature dependence of the formal potential of the ferricinium-ferrocene redox couple using a nonisothermal electrochemical cell arrangement in order to probe possible structural reasons for the limitations of the "ferrocene assumption" for estimating the transfer thermodynamics of single ions between different solvents. In contrast to the uniformly small positive values of $(\bar{S}^{\circ}_{Fc} - \bar{S}^{\circ}_{Fc^+})$ predicted by the Born model, the experimental quantities varied widely from small or even negative values in hydrogen-bonded solvents (-5 to 3 e.u.) to substantially larger values (11-14 e.u.) in dipolar aprotic media. These variations appear to arise chiefly from additional solvent ordering in the vicinity of the ferricinium cation compared to the ferrocene molecule which is enhanced in the aprotic solvents. The variations in $(\bar{S}^{\circ}_{Fc} - \bar{S}^{\circ}_{Fc^+})$ between water and a number of nonaqueous solvents provide a predominate contribution to the differences between the free energies of single ion transfer calculated using the ferrocene and alternative extrathermodynamic assumptions.

---

*Author to whom correspondence should be addressed.

Introduction

In recent years there has been a great deal of interest in developing methods by which the thermodynamics of transfer of single ions between various solvents ("medium effects") may be estimated.[1] All of these methods must involve some sort of extrathermodynamic assumption; the likely validity of the various proposed procedures has been extensively debated.[1,2] One such approach which has gained widespread popularity involves the assumption that the absolute standard potential ϕ_m° (the Galvani metal-solution potential difference) of the ferricinium-ferrocene (Fc^+/Fc) redox couple is independent of the solvent[1] (the "ferrocene assumption"). The method is particularly convenient for electrochemical determinations of the free energy of single ion transfer ΔG_t° since ΔG_t° can be estimated simply from the solvent effect upon the measured standard electrode potential for the appropriate cell reaction relative to the corresponding potentials for Fc^+/Fc under the same conditions. However, the use of the ferrocene assumption has been shown to yield significantly different estimates of ΔG_t° compared with those obtained by using other extrathermodynamic approaches, particularly when one of the solvents is water.[1-5] It has been suggested[2,5] that these discrepancies arise from variations in the specific solvation of the ferricinium cation between solvents which are not entirely compensated by corresponding changes in the solvation of the ferrocene molecule.

Measurements of the difference between the partial molal entropies of ferrocene and ferricinium ($\bar{S}_{Fc}^\circ - \bar{S}_{Fc^+}^\circ$) as a function of the solvent would provide a useful means of evaluating such differences in specific solvation
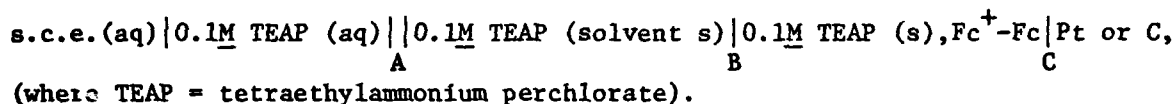
in view of the expected sensitivity of $\bar{S}^{\circ}$ to the degree of "solvent ordering" induced by the solute. Moreover, we have recently pointed out that such differences in $\bar{S}^{\circ}$ between the oxidized and reduced halves of redox couples [the "reaction entropy" $\Delta S^{\circ}_{rc} = (\bar{S}^{\circ}_{red} - \bar{S}^{\circ}_{ox})$] can be obtained to a good approximation (probably within 1 e.u.) from the temperature dependence of the formal electrode potential using a nonisothermal cell arrangement.[7] Although the evaluation of $(\bar{S}^{\circ}_{red} - \bar{S}^{\circ}_{ox})$ necessarily involves an extrathermodynamic assumption, in this case it is only required that the temperature coefficients of the thermal liquid junction potentials generated between the hot and cold parts of the cell are negligibly small. This condition is expected to be approximately fulfilled under most conditions.[7] The evaluation of $(\bar{S}^{\circ}_{red} - \bar{S}^{\circ}_{ox})$ in a given solvent therefore involves a much milder extrathermodynamic assumption than for the corresponding free energy difference $(\bar{G}^{\circ}_{red} - \bar{G}^{\circ}_{ox})$; the latter requires an *absolute* Galvani potential difference to be estimated, which is fraught with difficulties. The nonisothermal cell method has been utilized to obtain values of $(\bar{S}^{\circ}_{red} - \bar{S}^{\circ}_{ox})$ for a variety of substitutionally inert transition metal redox couples in aqueous[7,8] and nonaqueous media.[9] These reaction entropies have been found to be extremely sensitive to the nature of the ligands and the surrounding solvent which demonstrates the importance of short-range solvent polarization arising from specific ligand-solvent interactions to the solvation thermodynamics of metal complexes.[7-9]

In the present communication, values of $(\bar{S}^{\circ}_{Fc} - \bar{S}^{\circ}_{Fc^+})$ are reported in a range of solvents and compared with the corresponding predictions from the dielectric-continuum (Born) model in order to probe possible reasons for the suspected breakdown of the "ferrocene assumption" for estimating the transfer thermodynamics of single ions.

Experimental

Most solvents were Aldrich "Gold Label" grade and were used either following further drying with molecular sieves and vacuum distillation, or as received. Typical water content was $< 0.05\%$ as determined by Karl Fischer titration. Water was purified by "pyrodistillation".[7] Formal potentials E_f of the ferricinium-ferrocene couple were obtained by cyclic voltammetry using sweep rates in the range 50-500 mV sec^{-1}.[7] Platinum and/or vitreous carbon indicator electrodes were used. Reversible or quasi-reversible behavior was typically obtained in water, formamide, methanol, N-methyl formamide, propylene carbonate, acetonitrile, dimethyl sulfoxide, dimethylformamide, and nitromethane in that the separation between the anodic and cathodic voltammetric peaks was 60-80 mV with essentially equal peak currents. In most solvents, essentially identical formal potentials were obtained for either anodic-cathodic voltammograms using dissolved ferrocene, or cathodic-anodic voltammograms using ferricinium picrate as the solute. Indeed, we found that ferricinium is stable even in solvents of high basicity such as dimethylsulfoxide and dimethylformamide at temperatures up to 50°C for at least six hours, provided that the solutions were deaerated with nitrogen or argon and contained only weakly complexing anions such as perchlorate. These results are in contrast to earlier reports that ferricinium is rapidly decomposed in dimethylsulfoxide and dimethylformamide.[10] However, we observed that ferricinium decomposes in hexamethylphosphoramide even on the cyclic voltammetric timescale, as evidenced by reverse (cathodic-going) voltammetric peaks that were markedly smaller than the forward anodic peaks in this solvent using ferrocene as the solute. (Also, cyclic voltammetry of dissolved ferricinium in hexamethylphosphoramide yielded a wave only at a potential characteristic of the $Fe^{3+/2+}$ couple in this solvent.) In water,

ferricinium picrate was used as the solute on account of the limited solubility of ferrocene. No precipitation of electrogenerated ferrocene in the vicinity of the electrode appeared to occur during the period of the voltammetric scan in that cyclic voltammograms of reversible shape with equal anodic and cathodic peak currents were consistently obtained using ferricinium concentrations in the range 2×10^{-4} to 10^{-3} $\underline{M}$.

The values of ΔS°_{rc} for Fc^+/Fc in the various solvents were determined from the temperature dependence of E_f obtained from cyclic voltammetry using a nonisothermal cell arrangement similar to that described in Ref. 7. Electrode potentials were measured versus an aqueous s.c.e. (containing saturated NaCl rather than KCl to avoid precipitation of $KClO_4$ in the liquid junction) using the following configuration:

s.c.e.(aq)$|$0.1$\underline{M}$ TEAP (aq)$||$0.1$\underline{M}$ TEAP (solvent s)$|$0.1$\underline{M}$ TEAP (s),Fc^+-$Fc|$Pt or C,
$$\text{A}\text{B}\text{C}$$
(where TEAP = tetraethylammonium perchlorate).

The s.c.e. was held at room temperature and the temperature of the working compartment BC was varied over as wide a range as practicable (usually 30–60 deg.C); the thermal liquid junction[7] was formed within the region AB so that the unknown solvent liquid junction potential at A did not affect the temperature dependence of E_f. Following the arguments given or quoted in Ref. 7 for aqueous media, it is very likely that the temperature derivative of the thermal junction potential is negligible in comparison with (dE_f/dT). Since the "thermocouple" potential difference generated between the hot and cold regions of the platinum or carbon working electrode (or copper connecting leads) is also negligible,[7] then to a very good approximation

$(dE_f/dT) = (d\phi^\circ_m/dT)$ so that $\Delta S^\circ_{rc} = F(dE_f/dT)$. The resulting values of ΔS°_{rc} were found to be essentially independent (within the experimental reproducibility of ± 0.5–1 e.u.) of the ionic strength μ of the supporting electrolyte in the region AC for $0.01 \lesssim \mu \lesssim 0.5$, and when lithium perchlorate was substituted for TEAP.

Results and Discussion

Table I summarizes values of ΔS°_{rc} for the ferricinium-ferrocene couple, $(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})$, determined in nine solvents, along with the corresponding formal potentials measured at 25°C. Also listed in this table are the corresponding estimates of ΔS°_{rc}, $(\Delta S^\circ_{rc})_{Born}$, resulting from the dielectric-continuum Born model. Since according to the Born model $\Delta S^\circ_{rc} = -\bar{S}^\circ_{Fc+}$, these were evaluated using[12]

$$(\Delta S^\circ_{rc})_{Born} = -\frac{e^2 N}{2r\epsilon T}\left(\frac{d\ln\epsilon}{d\ln T}\right) \tag{1}$$

where r is the radius of the ferricinium cation, taken as 3.8 Å,[13] e is the electronic charge, N is Avogadro's number and ϵ is the dielectric constant of the solvent. (The literature sources for ϵ are given in the notes to Table I.)

In contrast to the Born estimates $(\Delta S^\circ_{rc})_{Born}$ which are uniformly small and positive (1-6 e.u.), the experimental reaction entropies are seen to increase markedly from a small *negative* value in water (-5 e.u.) to substantial positive values (11-14 e.u.) in several dipolar aprotic solvents. These results clearly indicate that there are significant differences in the nature and extent of solvent polarization between ferricinium and ferrocene that are sensitive to the microscopic solvent structure.

Criss and Salomon[14,15] have analyzed the available data for the ionic entropies $\bar{S}^\circ_+$ of simple univalent cations in various solvents in terms of the structural properties of the solvent. They noted that $\bar{S}^\circ_+$ for a given cation in various solvents generally becomes increasingly negative as the degree of "internal order" of the solvent (the degree of association between solvent molecules) decreases, suggesting that a major factor contributing to $\bar{S}^\circ_+$ is the extent to which the cation can induce additional solvent order within its

vicinity.[14] The decreases in $\bar{S}^\circ_+$ generally found for the transfer of a given cation from water to other solvents have been found to be given by a characteristic "a" parameter for each solvent, where the value of "a" decreases as the internal order of the solvent decreases.[14,15] These "a" parameters are also listed in Table I. It is seen that the experimental increases in $(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})$ in going from water to the other solvents do roughly parallel the corresponding "a" values in most solvents, as would be expected if $\bar{S}^\circ_{Fc+}$ varies with the solvent in a similar manner to $\bar{S}^\circ_+$ for simple univalent cations, and if $\bar{S}^\circ_{Fc}$ is not strongly dependent on the solvent. (Significant variations in $\bar{S}^\circ_{Fc}$ may occur, but will be of no consequence to the validity of the ferrocene assumption as long as they are accompanied by comparable variations in $\bar{S}^\circ_{Fc+}$.) Thus small values of $(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})$ were obtained for solvents such as water, formamide, and N-methylformamide that are expected to be polymerized to some extent via hydrogen bonding.[14] Markedly larger values were observed for the aprotic solvents propylene carbonate, acetonitrile, dimethylsulfoxide, dimethylformamide, and nitromethane; these have a low degree of internal order[14,15] but have sizable dipole moments which should encourage solvent ordering in the vicinity of ferricinium by means of ion-dipole interactions. It is interesting to note that the variations of $(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})$ for the most part do not correlate with the expected basicity of the solvent, as measured for example by the so-called solvent "donor number" DN[16] (Table I). A similar finding has been noted previously for monoatomic cations.[15]

The small *negative* value of $(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})$ in water has been noted previously.[8] This unexpected result has been ascribed to the delocalization of the reducing electron around the cyclopentadienyl rings leading to a net *increased* polarization of adjacent water molecules in the lower oxidation state.[8] The enhancement of the water structure from the hydrophobic nature of the ferrocene molecule ("solvation of the second kind")[5,6] may also be a factor along with

the involvement of quadrupole-dipole interactions.[6] Such solvent polarization around the neutral ferrocene molecule may also occur in the other solvents, but is presumably outweighed by the greater tendency of the ferricinium cation to induce solvent ordering via ion-dipole interactions. In any case, the ferrocene assumption is clearly unsuited for estimating entropies of single ion transfer between different solvents, especially involving water or other hydrogen-bonded solvents.

In view of the substantially larger observed variations in ΔS°_{rc} in changing from water to other solvents, $\Delta(\Delta S^{\circ}_{rc})^{s-w}$, compared with the corresponding dielectric-continuum predictions $\Delta(\Delta S^{\circ}_{rc})^{s-w}_{Born}$, it is of interest to compare these experimental results with the disparities noted previously between the values of transfer free energies for single ions ΔG°_{t} obtained using the ferrocene and alternative extrathermodynamic assumptions.[1] Of the numerous methods devised so far, aside from the ferrocene procedure the most widely accepted approaches are: (1) the "tetraphenylarsonium - tetraphenylborate" ("Ph$_4$AsPh$_4$B") procedure, which assumes that $\Delta G^{\circ}_{t}(Ph_4As^+) = \Delta G^{\circ}_{t}(Ph_4B^-) = 0.5\Delta G^{\circ}_{t}(Ph_4AsPh_4B)$; and (2) the "zero liquid junction potential" procedure, which assumes that the net liquid junction potential between a pair of solvents is negligible when 0.1 $\underline{M}$ tetraethylammonium picrate dissolved in either solvent is used as the salt bridge.[1] Methods (1) and (2) have been shown to yield consistently similar values of ΔG°_{t} (usually within ca 1 kcal mole^{-1}) between a wide range of solvents.[1,17] However, the values of ΔG°_{t} for ion transfer from water to other solvents, $(\Delta G^{\circ}_{t})^{s-w}_{Fc}$, obtained using the ferrocene procedure have been found to be consistently less positive than the corresponding values, $(\Delta G^{\circ}_{t})^{s-w}_{1}$ and $(\Delta G^{\circ}_{t})^{s-w}_{2}$, obtained using methods (1) and (2), respectively. Assuming for the moment that methods (1) and (2) yield the "true" transfer free energy $(\Delta G^{\circ}_{t})^{s-w}_{true}$, the alteration in the free energy difference $(\bar{G}^{\circ}_{Fc} - \bar{G}^{\circ}_{Fc^+})$ between ferrocene and ferricinium upon transfer from water to another solvent,

$\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc+})^{S-W}$, can be obtained from

$$\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc+})^{S-W} \approx (\Delta G^\circ_t)^{S-W}_{Fc} - (\Delta G^\circ_t)^{S-W}_{true} \qquad (2)$$

Table II consists of estimates of $\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc+})^{S-W}$ obtained using eqn (2) from values of ΔG°_t for Ag^+ and Cu^{2+} tabulated in Refs. 1 and 2, along with the corresponding values of $T\Delta(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})^{S-W}$ extracted from the data given in Table I. It is seen that the increasing values of $-\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc+})^{S-W}$ obtained for solvents of decreasing structure and ionizing ability are typically par-alleled by comparable or larger values of $T\Delta(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})^{S-W}$, although inevitably there are some disparities in the estimates of $\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc+})^{S-W}$ obtained using methods (1) and (2). Since the values of $T\Delta(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})^{S-W}$ do not rely criti-cally on any particular extrathermodynamic assumption, this finding can be taken as additional evidence that methods (1) and (2) are indeed more trust-worthy than the ferrocene assumption. If the estimates of $\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc+})^{S-W}$ by either method (1) or (2) are approximately correct, then from the data in Table II it follows that typically $-\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc+}) \sim T\Delta(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc+})$; i.e., that $\Delta(\bar{H}^\circ_{Fc} - \bar{H}^\circ_{Fc+}) \sim 0$. This suggests that a primary reason for the probable break-down of the ferrocene assumption is simply the greater tendency of solvent dipoles to be polarized by the ferricinium cation compared with the ferrocene molecule, to an extent which is greater than predicted from the Born model and sensitive to the microscopic structure of the solvent. Parallel, although larger, variations in ΔS°_{rc} upon altering the nature of the solvent have also been seen for a number of substitutionally inert transition-metal redox couples carrying multiple charges which emphasize the importance of specific ligand-solvent interactions to their thermodynamics.[9] These findings also have important implications for understanding the influence of solvent reorganiza-tion upon the kinetics of outer-sphere electron transfer.[9]

Acknowledgement

References

(1) For a recent review, see O. Popovych, "Treatise on Analytical Chemistry", I. M. Kolthoff, P. J. Elving (eds), Part I, Vol I, 2nd ed., Wiley, N.Y., 1978, p. 271.

(2) J. F. Coetzee, W. K. Istone, Anal. Chem. $\underline{52}$, 53 (1980).

(3) J. F. Coetzee, J. J. Campion, J. Am. Chem. Soc. $\underline{89}$, 2513 (1967).

(4) I. M. Kolthoff, M. K. Chantooni, Jr., J. Phys. Chem. $\underline{76}$, 2024 (1972).

(5) J. W. Diggle, A. J. Parker, Electrochim. Acta $\underline{18}$, 975 (1973).

(6) M. Alfenaar, J. Phys. Chem. $\underline{79}$, 2200 (1975).

(7) E. L. Yee, R. J. Cave, K. L. Guyer, P. D. Tyma, M. J. Weaver, J. Am. Chem. Soc. $\underline{101}$, 1131 (1979).

(8) E. L. Yee, M. J. Weaver, Inorg. Chem., $\underline{19}$, 1077 (1980).

(9) S. Sahami, M. J. Weaver, submitted for publication.

(10) P. Prins, A. R. Korsuragen, A. G. T. G. Kortbeek, J. Organometallic Chem. $\underline{39}$, 335 (1972); A. Horsfield, A. Wassermann, J. Chem. Soc. Dalton, 187 (1972).

(11) A. J. de Bethune, T. S. Licht, N. Swendeman, J. Electrochem. Soc. $\underline{106}$, 616 (1959).

(12) See for example, R. M. Noyes, J. Am. Chem. Soc. $\underline{84}$, 513 (1962).

(13) D. R. Stranks, Disc. Far. Soc. $\underline{29}$, 73 (1960).

(14) C. M. Criss, M. Salomon, in "Physical Chemistry of Organic Solvent Systems", A. K. Covington, T. Dickinson (eds), Plenum, 1973, pp. 290-298.

(15) C. M. Criss, J. Phys. Chem. $\underline{78}$, 1000 (1974).

(16) V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions", Plenum, N. Y., 1978, pp. 19-27.

(17) R. Alexander, A. J. Parker, J. H. Sharp, W. E. Waghorne, J. Am. Chem. Soc. $\underline{94}$, 1148 (1972).

TABLE I. $\Delta S^{\circ}_{rc}(=\bar{S}^{\circ}_{Fc} - \bar{S}^{\circ}_{Fc^+})$ for the Ferricinium-Ferrocene Redox Couple in Various Solvents. Comparison with Predictions from Born Model.

Solvent	E_f[a]	ΔS°_{rc}[b]	$(\Delta S^{\circ}_{rc})_{Born}$[c]	$-a$[d]	D.N.[e]
	vs s.c.e.	cal deg^{-1}mol^{-1}	cal deg^{-1}mol^{-1}	cal deg^{-1}mol^{-1}	
Water	127	-5	2.5[f]	0.0	~18
Formamide	245	0	1.3[g]	1.5	~24
Methanol	346	3	6.4[h]	10.8	19
N-Methylformamide	334	4	2.0[g]	4.8	
Propylene Carbonate	270	11	2.6[j]	9.3	15
Acetonitrile	309	11.5	4.9[i]	18.3	14
Dimethylsulfoxide	317	12.5	3.3[i]	9.9	30
Dimethylformamide	363	13.5	5.7[g]	15.9	26.5
Nitromethane	270	14	5.0[k]	--	2.7

Notes for Table I.

[a] Formal potential of Fc^+/Fc in 0.1 $\underline{M}$ TEAP in listed solvent at 25°C,

determined by cyclic voltammetry (see text); potentials quoted versus aqueous

s.c.e. (filled with saturated NaCl) using cell:

   Na sce(aq)|0.1$\underline{M}$ TEAP (aq)||0.1$\underline{M}$ TEAP (solvent)|Pt or C   [The Na s.c.e.

has a potential in contact with 0.1 $\underline{M}$ TEAP that is +5 mV. versus the conven-

tional s.c.e. filled with saturated KCl.]

[b] Reaction entropy of Fc^+/Fc in listed solvent at 25°C; obtained from tempera-

ture dependence of E_f using nonisothermal cell arrangement (see text and

Ref. 7 for details). Experimental precision ca. ±0.5-1 e.u.

[c] Value of ΔS°_{rc} at 25°C predicted from the Born model; calculated from eqn (1)

using dielectric constant data from literature sources indicated.

[d] Empirical "a" parameter describing dependence of $\bar{S}^\circ_+$ upon solvent, from Ref. 15.

[e] "Donor number" of solvent, from Ref. 16.

  Literature sources for dielectric constants: [f] Ref. 12.

[g] S. J. Bass, W. I. Nathan, R. M. Meighan, R. H. Cole, J. Phys. Chem. <u>68</u>,

  509 (1964).

[h] P. G. Sears, R. R. Holmes, L. R. Dawson, J. Electrochem. Soc. <u>102</u>, 145 (1955).

[i] G. J. Janz, R. P. T. Tomkins, "Nonaqueous Electrolyte Handbook", Vol. I.,

  Academic Press, N.Y., 1972.

[j] R. Payne, I. E. Theodorou, J. Phys. Chem. <u>76</u>, 2892 (1972).

[k] C. P. Smyth, W. S. Walls, J. Chem. Phys. <u>3</u>, 557 (1935).

TABLE II. Estimates of transfer free energies for ferricinium-ferrocene redox couple from water to various other solvents $\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc^+})^{s-w}$ obtained using eqn (2), compared with corresponding transfer entropies $T(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc^+})^{s-w}$ for T = 25°C.

Solvent	$-\Delta(\bar{G}^\circ_{Fc} - \bar{G}^\circ_{Fc^+})^{s-w}$,[a] kcal mol^{-1}			$T\Delta(\bar{S}^\circ_{Fc} - \bar{S}^\circ_{Fc^+})$,[f]
	Method (1)[b,d]	Method (2)[b,e]	Method (2)[c,e]	kcal mol^{-1}
Formamide	1.1	2.0	–	1.5
Propylene Carbonate	1.8	3.3	3.4	4.7
Dimethylsulfoxide	2.6	3.0	2.8	5.0
Dimethylformamide	2.7	3.7	4.1	5.8
Acetonitrile	3.1	4.2	5.6	4.9
Methanol	4.6	5.0	7.5	2.4

Notes for Table II.

a Variation in $(\bar{G}^{\circ}_{Fc} - \bar{G}^{\circ}_{Fc}+)^{s-w}$ in changing from water to solvent listed; estimated from eqn (2) using method indicated.

b From eqn (2), using ion transfer energies for Ag^+ calculated from data in Table 12VI of Ref. 1.

c From eqn (2), using ion transfer energies for Cu^{2+} from Table VI of Ref. 2.

d Values of $(\Delta G^{\circ}_t)^{s-w}_{true}$ assumed to equal those given by "Ph$_4$AsPh$_4$B assumption" [Method (1); see text].

e Values of $(\Delta G^{\circ}_t)^{s-w}_{true}$ assumed to equal those given by "zero liquid junction potential assumption" [Method (2); see text].

f Variation in $(\bar{S}^{\circ}_{Fc} - \bar{S}^{\circ}_{Fc}+)$ in changing from water to solvent listed; obtained from values given in Table I for ionic strength $\mu=0.1$.